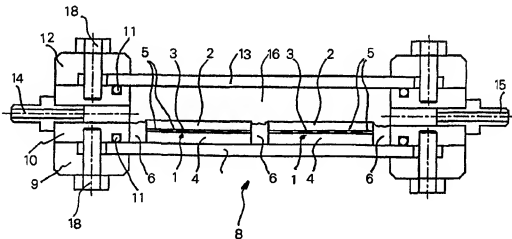




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(21) International Application Number: PCT/NL99/00731 (22) International Filing Date: 30 November 1999 (30.11.99) (30) Priority Data: 1010787 11 December 1998 (11.12.98) NL (71) Applicant (for all designated States except US): STICHTING ENERGIEONDERZOEK CENTRUM NEDERLAND [NL/NL]; Postbus 1, NL-1755 ZG Petten (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): WIENKE-ULLRICH, Jeannette, Angela [DE/NL]; Henriëtte Roland Holststraat 34, NL-1827 LR Alkmaar (NL). SPÄTH, Martin [DE/NL]; Voorburggracht 55, NL-1722 GD Zuid-Scharwoude (NL). (74) Agent: DOKTER, Hendrik, Daniël; Octrooibureau Dokter & Mink, P.O. Box 657, NL-7300 AR Apeldoorn (NL).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>In English translation (filed in Dutch).</i>

(54) Title: LIQUID-CONTAINING SOLAR CELL AND SOLAR PANEL ASSEMBLED THEREWITH



(57) Abstract

Liquid-containing solar cell comprising a layered structure of at least one working electrode formed by a first electrically conductive layer and a photovoltaically operating layer arranged on the first electrically conductive layer, a counter-electrode coupled mechanically to the working electrode and formed by a second electrically conductive layer, and an electrolytic medium held between the working electrode and counter-electrode, wherein at least one of the electrically conductive layers is transparent and deposited on a transparent substrate, wherein at least one side of the solar cell is adapted to receive sunlight, wherein cooling means are provided for cooling the electrolytic medium, and photovoltaic solar panel comprising a plate-like carrier which is provided with at least two such solar cells.

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LIQUID-CONTAINING SOLAR CELL AND SOLAR PANEL ASSEMBLED
THEREWITH

The invention relates to a liquid-containing solar cell comprising a layered structure of at least one working electrode formed by a first electrically conductive layer and a photovoltaically operating layer arranged on the first electrically conductive layer, a counter-electrode coupled mechanically to the working electrode and formed by a second electrically conductive layer, and an electrolytic medium held between the working electrode and counter-electrode, wherein at least one of the electrically conductive layers is transparent and deposited on a transparent substrate.

Such a solar cell is known from the International patent application WO 91/16719.

The known solar cell comprises a light-transmitting electrically conductive layer which is deposited on a glass plate or a transparent polymer foil to which a number of preferably porous layers of titanium dioxide have been applied and wherein at least the last titanium dioxide layer is doped with a divalent or trivalent metal ion. The combination of titanium dioxide and conductive layer forms the working electrode of a solar cell, which solar cell further comprises a light-transmitting second electrically conductive layer which is deposited on a light-transmitting substrate and which forms a counter-electrode. Received between working electrode and counter-electrode is an electrolyte containing a redox system. Applied to the surface of the titanium dioxide layer is a sensitizer dye containing a di- or trivalent metal ion. The operation of the known solar cell is as follows. A photon from the visible part of the solar spectrum incident via the working electrode is absorbed by the dye, wherein this dye acquires an energy-rich state and is able to inject an electron with an efficiency of almost 100%

into the conduction band of the titanium dioxide, which electron is discharged via the electrically conductive layer of the photoelectrode. The resulting hole is supplemented with an electron from the electrolyte, while
5 the electrolyte accepts an electron from the counter-electrode. The acceptance of electrons by the electrolyte can be enhanced by a catalyst applied to the surface of the counter-electrode.

Such a known solar cell has a number of
10 disadvantageous properties which form an obstacle to use of the cell in the outside air and thereby stand in the way of large-scale application of this cell. Inherent to the exposure to sunlight of an electrolytic liquid enclosed in a space between two electrodes is the danger
15 of this liquid leaking out due to cracks occurring in the walls bounding the space as a result of the expansion of the liquid, or the risk of the liquid boiling. Even in cases where the liquid does not boil or leak, temperature increase results in a decreased efficiency of the solar
20 cell.

It is an object of the invention to provide a liquid-containing solar cell which is free of said drawbacks.

This object is achieved, and other advantages gained, with a solar cell of the type stated in the preamble,
25 wherein according to the invention cooling means are provided for cooling the electrolytic medium.

The cooling means are for instance adapted to guide a fluid along and in contact with the side of the solar cell opposite the side adapted to receive sunlight, in other
30 words (according to the terminology usual in the field) along and in contact with the rear side of the solar cell. (The side adapted to receive sunlight is referred to in the field as the front side).

In an embodiment of a solar cell according to the
35 invention wherein the fluid is guided along and in contact with the rear side of the solar cell, the first electrically conductive layer is transparent and is

deposited on a surface of a transparent substrate, the opposite surface of which forms the side adapted to receive sunlight, i.e. the front side of the solar cell. The electrolytic medium in such a solar cell is situated
5 for a small part in and for the greater part beneath the metal oxide semiconductor material on the rear side of the solar cell and is cooled via the second electrically conductive layer by the fluid flowing beneath this layer.

In a following embodiment of a solar cell according
10 to the invention wherein the fluid is guided along and in contact with the rear side of the solar cell, the second electrically conductive layer is transparent and is deposited on a surface of a transparent substrate, the opposite surface of which forms the side adapted to
15 receive sunlight, i.e. the front side of the solar cell. Such a solar cell is known under the name "reversed dye-sensitized solar cell" or "reversed dye solar cell". The electrolytic medium in such a reversed dye solar cell is situated for the greater part beneath the second
20 electrically conductive layer on the front side and for a small part in the metal oxide semiconductor material on the rear side of the solar cell and is cooled via the metal oxide semiconductor material and the first electrically conductive layer by the fluid flowing beneath
25 this layer.

In advantageous manner the cooling means are for instance adapted to guide a fluid along and in contact with the side of the solar cell adapted to receive sunlight, in other words along and in contact with the
30 front side of the solar cell.

In an embodiment of a solar cell according to the invention wherein the fluid is guided along and in contact with the front side of the solar cell, the first electrically conductive layer is transparent and is
35 deposited on a surface of a transparent substrate, the opposite surface of which forms the side adapted to receive sunlight, in other words the front side of the

solar cell. The electrolytic medium in such a solar cell is situated for a small part in and for the greater part beneath the metal oxide semiconductor material on the rear side of the solar cell and is cooled via the metal oxide
5 semiconductor material, the first electrically conductive layer and the substrate therefor by the fluid flowing through this substrate.

In a following embodiment of a solar cell according to the invention wherein the fluid is guided along and in
10 contact with the front side of the solar cell, the second electrically conductive layer is transparent and is deposited on a surface of a transparent substrate, the opposite surface of which forms the side adapted to receive sunlight, in other words the front side of the
15 solar cell. The electrolytic medium in such a reversed dye solar cell is situated for the greater part beneath the second electrically conductive layer on the front side and for a small part in the metal oxide semiconductor material on the rear side of the solar cell and is cooled via the
20 second electrically conductive layer and the substrate therefor by fluid flowing through this substrate.

In embodiments wherein the fluid flows along the front side and when electrically insulating substrates of suitable types of glass or plastic are used, this fluid
25 does not come into contact with voltage-carrying parts of the solar cell, so that without problem the fluid can for instance be water. More particularly the fluid can be salt water, which offers great advantages for instance in large-scale application in regions where clean water is
30 scarce.

The counter-electrode in a solar cell according to the invention can in per se known manner be mechanically coupled to the counter-electrode, for instance using an O-ring.

35 In an advantageous embodiment of the solar cell according to the invention, it is provided along its periphery with a vapour and liquid-tight peripheral edge

of a suitably chosen plastic material, for instance an adhesive material based on an MS polymer, which has favourable shrinkage properties and a good UV resistance and requires little pre-treatment, so that it is easy to process.

It has been found that with such an adhesive material a reliable, strong and durable liquid- and gas-tight sealing of the solar cell is obtained, even under extreme conditions of temperature and pressure.

The advantages of said adhesive material are utilized still further in an embodiment in which it has a substantially white colour, which results in an increase in the number of reflections of incident sunlight and therewith in an increase in the efficiency of the solar cell.

The invention further relates to a photovoltaic solar panel, comprising a plate-like carrier which is provided with at least two solar cells according to the above described invention.

The advantages of the invention are particularly manifest in a solar panel in which the solar cells are received in a housing which is formed by a standing peripheral edge of the carrier and a transparent cover plate connecting onto this peripheral edge and extending over the side of the solar cells adapted to receive sunlight, which housing is provided with at least an inlet and an outlet for guiding a fluid along and in direct contact with the solar cells.

The fluid in such a solar panel comes into direct contact with the solar cells thereof, which results in a value for the refractive index at a transition fluid/solar cell of incident light resulting in a more effective conversion of light into electrical current than the refractive index at a transition air/solar cell in a prior art solar panel.

A panel according to the invention can be adapted to the requirements of the user, for instance by adjusting

the distance between the cover plate and the solar cells, and thereby the thickness of the fluid layer above the solar cells and/or the flow rate of the fluid through the housing, to the desired temperature gradient to be realized over the fluid layer.

By adding suitably chosen substances to the fluid or by using a cover plate with a suitable coating, a filter for determined wavelength bands in the incident ultraviolet light is obtained in simple manner, which prevents undesired effects in the working electrode, for instance destructive optical excitation of the semiconductor material of the working electrode.

The invention will be elucidated hereinbelow on the basis of an embodiment with reference to the drawing.

In the drawing fig. 1 and 2 show an embodiment of a solar panel according to the invention in respectively top view and front view.

Fig. 1 shows a solar panel 8 with the side adapted to receive sunlight facing upward, fig. 2 shows the solar cell 8 in a front view through the cross-section along the line II-II of fig. 1. Panel 8 contains ten solar cells 1 connected electrically in parallel, each comprising a layered structure of a working electrode, composed of a transparent electrically conductive layer (not shown) of a per se known suitable material (for instance a so-called TCO layer, i.e. a layer of a transparent conductive oxide material), on a transparent glass substrate 2. In the example a group of five cells 1 at a time is integrated on a joint substrate 2. On the transparent electrically conductive layer a layer 3 of nanocrystalline TiO_2 is deposited per solar cell 1, wherein an edge zone of the conductive layer remains uncovered on two opposite sides of the TiO_2 layer. The TiO_2 is provided with a suitable sensitizer material of a per se known type. Coupled to the working electrode by means of adhesive edges 5 of a known material is a counter-electrode composed of an electrically conductive layer of a per se known suitable

material on a substrate 4 suitable for this purpose. A lithium iodide/iodine-containing mixture is held as electrolytic medium in the spaces between the working electrodes and the respective counter-electrode. Applied to the conductive layer of the counter-electrode is a thin graphite layer which serves as catalyst for the conversion in the electrolyte of I_3^- to I^- . The working electrodes are coupled in each case to the respective counter-electrodes using an adhesive edge 5 between the respective substrates of working electrode and counter-electrode of a material which is resistant to the electrolytic medium. Solar cells 1 are each provided along their sides not adjoining another cell with a vapour- and liquid-tight peripheral edge 6 of an adhesive material based on an MS polymer having a substantially white colour. Substrates 4 are fixed to a carrier plate 7 which is clamped in between a lower frame 9 and an intermediate frame 10 which is provided on its underside with a groove for an O-ring 11 for liquid- and gas-tight sealing of carrier plate 7. Between the intermediate frame 10 and an upper frame 12 a cover plate 13 of a transparent material is clamped in liquid- and gas-tight manner into a groove in the underside of upper frame 12 using an O-ring 11. Solar cells 1 are cooled during operation with cooling water which is supplied through the intermediate frame 10 via inlets 14 into the space 16 between cover plate 13 and substrates 2, and which flows over solar cells 1 and which is drained on the opposite side via outlets 15 through the intermediate frame 10. The figure further shows electrical connections 17 for transporting current generated by cells 1 and screws 18 with which lower frame 9 and upper frame 12 are fixed to intermediate frame 10.

With a solar cell, and in particular a solar panel according to the invention a device is provided which can be installed simply on roofs and houses for generating electricity, the appearance of which can be adapted to

colour variations in the surroundings by a suitable choice of cover plate and cooling liquid.

Due to the use of a transparent cover plate in a panel according to the invention this panel is highly
5 suitable for integration in or placing on the roof of greenhouses and glasshouses for glass horticulture.

The conduit system for the applied fluid, in particular water, can for instance be coupled to installations for heating, hydrolysis or desalination, for
10 instance for use in swimming pools.

CLAIMS

1. Liquid-containing solar cell (1) comprising a layered structure of at least one working electrode (2, 3) formed by a first electrically conductive layer and a photovoltaically operating layer (3) arranged on the first electrically conductive layer, a counter-electrode (4) coupled mechanically to the working electrode (2, 3) and formed by a second electrically conductive layer, and an electrolytic medium held between the working electrode (2, 3) and counter-electrode (4), wherein at least one of the electrically conductive layers is transparent and deposited on a transparent substrate (2), wherein at least one side of the solar cell is adapted to receive sunlight, **characterized in that** cooling means (14, 15, 16) are provided for cooling the electrolytic medium.
2. Solar cell as claimed in claim 1, **characterized in that** the cooling means (14, 15, 16) are adapted to guide a fluid along and in contact with the side of the solar cell opposite the side adapted to receive sunlight.
3. Solar cell as claimed in claim 2, **characterized in that** the first electrically conductive layer is transparent and is deposited on a surface of a transparent substrate, the opposite surface of which forms the side of the solar cell adapted to receive sunlight.
4. Solar cell as claimed in claim 2, **characterized in that** the second electrically conductive layer is transparent and is deposited on a surface of a transparent substrate, the opposite surface of which forms the side of the solar cell adapted to receive sunlight.
5. Solar cell (1) as claimed in claim 1, **characterized in that** the cooling means (14, 15, 16) are adapted to guide a fluid along and in contact with the side of the solar cell (1) adapted to receive sunlight.

6. Solar cell (1) as claimed in claim 5, characterized in that the first electrically conductive layer is transparent and is deposited on a surface of a transparent substrate (2), the opposite surface of which
5 forms the side of the solar cell adapted to receive sunlight.

7. Solar cell as claimed in claim 5, characterized in that the second electrically conductive layer is transparent and is deposited on a surface of a transparent
10 substrate, the opposite surface of which forms the side of the solar cell adapted to receive sunlight.

8. Solar cell as claimed in claim 5, characterized in that the fluid contains substances acting as selective UV filter and selectively absorbing ultraviolet light.

15 9. Solar cell (1) as claimed in any of the claims 2-8, characterized in that the fluid is water.

10. Solar cell (1) as claimed in any of the foregoing claims, characterized in that it is provided along its periphery with a vapour and liquid-tight peripheral edge
20 (6) of a suitably chosen plastic material.

11. Solar cell (1) as claimed in claim 10, characterized in that the plastic material is an adhesive material (6) based on an MS polymer.

12. Solar cell (1) as claimed in claim 10,
25 characterized in that the adhesive material (6) has a substantially white colour.

13. Photovoltaic solar panel (8), comprising a plate-like carrier (7) which is provided with at least two solar cells (1) as claimed in any of the foregoing claims.

30 14. Solar panel (8) as claimed in claim 13, characterized in that the solar cells (1) are received in a housing (7, 9, 10, 12, 13) which is formed by a standing peripheral edge (10) of the carrier (7) and a transparent cover plate (13) connecting onto this peripheral edge (10)
35 and extending over the side of the solar cells (1) adapted to receive sunlight, which housing (7, 9, 10, 12, 13) is provided with at least an inlet (14) and an outlet (15)

for guiding a fluid along and in direct contact with the solar cells (1).

15. Solar panel (8) as claimed in claim 14,
characterized in that the transparent cover plate (13)
5 contains substances acting as selective UV filter and
selectively absorbing ultraviolet light.

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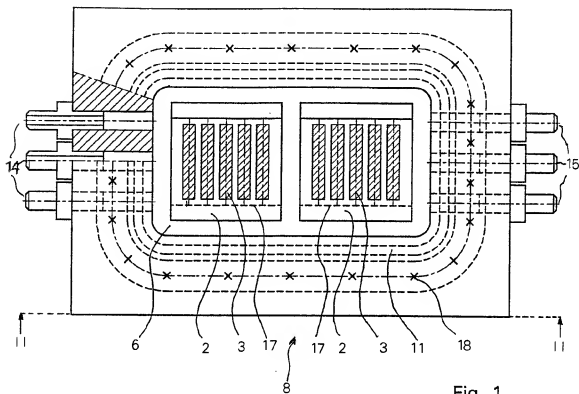


Fig. 1

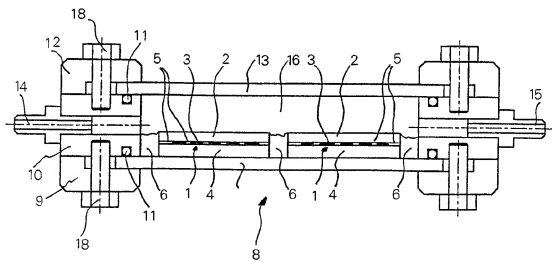


Fig. 2

INTERNATIONAL SEARCH REPORT

Inter: Application No
PCT/NL 99/00731

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01G9/20 H01L31/052

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L H01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 855 726 A (LECLANCHE SA) 29 July 1998 (1998-07-29) column 5, line 15 - column 7, line 44; figure 5	1-9, 13, 14
Y	US 4 052 228 A (RUSSELL CHARLES R) 4 October 1977 (1977-10-04) column 2, line 32 - column 4, line 2; figure 6	1-9, 13, 14
A	EP 0 789 405 A (TOYOTA MOTOR CO LTD) 13 August 1997 (1997-08-13) page 3, line 47 - line 56 page 5, line 30 - line 44; figure 1 -/-	1, 2, 5, 8, 9, 13-15

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>SPÄTH, M. ET AL.: "New concepts of nano-crystalline organic photovoltaic devices" 1997 IEEE 26TH PHOTOVOLTAIC SPECIALISTS CONFERENCE, 30 September 1997 (1997-09-30) - 3 October 1997 (1997-10-03), pages 503-506, XP002109862 Anaheim, CA page 504, column 2, line 15 -page 505, column 1, line 2; figures 1,3,4</p>	1-4

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter Application No
PCT/NL 99/00731

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0855726	A	29-07-1998	NONE	
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